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(54) Title: PROCESSES FOR PREVENTING GENERATION OF HYDROGEN HALIDES IN AN OLIGOMERIZATION PROD-
UCT RECOVERY SYSTEM

(57) Abstract: The invention is an oligomerization process. A catalyst, a lower olefin, and a process medium are provided. The lower olefin is reacted in the presence of the catalyst to produce a product stream comprising a higher olefin product and a catalyst residue dispoersed in the process medium. The resulting product stream is treated with a quenching material. The quenching material can be an aliphatic primary amine, an aliphatic secondary amine, an alcohol, or a combination of those materials. Amine quenching materials have been found to generate few or no hydrogen halides when used to quench oligomerization catalysts. Alcohol quenching materials can generate hydrogen halides in use. This problem can be alleviated by treating the product stream with a stabilizing material that forms a stable hydrogen halide salt. Exemplary stabilizing materials include aliphatic amines, aromatic amines, and metal salts of amides, butoxides, or carboxylic acids.

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PROCESSES FOR PREVENTING GENERATION OF HYDROGEN
HALIDES IN AN OLIGOMERIZATION PRODUCT RECOVERY SYSTEM
BACKGROUND OF THE INVENTION

This invention relates generally to the catalytic production of olefins.

5 This invention relates more specifically to a process of quenching the catalyst in the effluent from an oligomerization reactor, such as a trimerization reactor, to avoid the generation of hydrogen halides.

Olefins, particularly alpha-olefins, also referred to as 1-olefins, have many uses as specific chemicals and as monomers or co-monomers in poly-
10 merization processes. Higher alpha-olefins and other olefins can be produced by contacting lower olefins, for example ethylene, with a catalyst, producing trimers of mono-olefins, dimers of diolefins, or other reaction products in an addition reaction. This reaction can be referred to as "trimerization" or "oligomerization". Often, the catalyst system is dispersed in a process solvent, and the reactants, a lower 1-olefin
15 and optionally hydrogen, are fed in as gases. The reaction product or higher olefins dissolve in the process solvent as they are formed.

Product olefins and spent catalyst system are recovered by removing the process solvent containing them, i.e. the reactor effluent, from the reactor. Preferably, a catalyst kill agent is added to the reaction system prior to separating
20 any of the reaction components. The effluent can be treated to quench or "kill" the catalyst. The effluent can be separated for catalyst system waste disposal, recycle any remaining lower 1-olefin and process solvent content, and recover product olefins.

A quenching agent can be used to quench the aluminum alkyl portion
25 of the catalyst system. Quenching of the catalyst system is important to prevent isomerization of the 1-olefin product to undesirable internal, i.e. 2- and higher, olefins, which lowers the product purity. Quenching of the catalyst system also can remove hazards associated with the air- and water- sensitive aluminum alkyls.

Previous patents teach that an alcohol can be added to the catalyst
30 discharge in the effluent of an olefin oligomerization reactor to quench or "kill" the catalyst. U.S. Patent No. 5,689,028 discloses adding 2-ethylhexanol to the reactor effluent of a trimerization reactor as a quenching agent to quench the catalyst

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system. U.S. Patent No. 5,859,303, Example 1, discloses that addition of an alcohol can quench or kill the catalyst system. U.S. Patent No. 5,750,817 discloses the use of ethanol to quench an ethylene trimerization reaction.

U.S. Patent No. 5,750,816 teaches the addition of alcohols, phenols,
5 carboxylic acids, primary or secondary amines, or ammonia to the effluent of an ethylene trimerization reactor as a "metal solubilizing agent". The patent states, "the percentage of the metal solubilizing agent used may be selected from a wide range from a trace amount to a solvent equivalent, but it is preferably in a range from 0.001 to 50% by weight, more preferably 0.01 to 10% by weight in terms of
10 concentration in the solvent". For example 0.022% by weight 1-hexanol (Examples 5 and 13), hexylamine (Examples 6 and 14), or ammonia (Examples 7 and 15) is used. The patent teaches generally that this step "maintain[s] the dispersed state of principally the catalyst components in the reaction dispersion" "in the process line from the outlet of the oligomerization reactor to the inlet of the distillation tower."
15 U.S. Patent No. 5,750,816, col. 12, lines 20-23 and 49-67.

SUMMARY OF THE INVENTION

The present inventors have discovered that alcohols, used as quenching agents to quench a halogenated trimerization catalyst system, following an oligomerization reaction, can produce hydrogen halides. For example, quenching
20 a chlorinated catalyst with an alcohol, particularly in the presence of water or the kettle bottoms found in a plant (which may contain ferrous chloride), may lead to the production of hydrogen chloride gas. Hydrogen halides can be highly corrosive to process equipment.

Accordingly it is desirable to provide catalyst quenching materials
25 and methods that do not produce hydrogen halides.

Again it is desirable to reduce or eliminate the generation of hydrogen halides when alcohols are used as quenching agents.

One or more of the preceding desires, or one or more other desires which will become plain upon consideration of the present specification, are
30 satisfied in whole or in part by the invention described here.

One aspect of the invention is an oligomerization process. In the process a catalyst system, a lower olefin reactant, and a process medium are

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provided. The lower olefin is reacted in the presence of the catalyst system to produce a product stream. The product stream includes a higher olefin product and catalyst system residue, both dispersed in the process solvent or medium.

The resulting product stream is treated with a quenching material comprising an aliphatic primary amine, an aliphatic secondary amine, or a combination of those materials. Optionally, an alcohol or other quenching materials also can be combined with the selected amine to form composite quenching materials. The quenching material is provided in an amount at least substantially effective to quench the catalyst.

Amine quenching materials have been found to generate few or no hydrogen halides when used to quench oligomerization catalysts.

Another aspect of the invention is an oligomerization process in which the product stream is treated with an alcohol in an amount at least partially effective to quench the catalyst. The product stream is also treated with a stabilizing material that forms a stable hydrogen halide salt. The stabilizing material is provided in an amount effective to at least reduce the generation of free hydrogen halides.

Although alcohol quenching materials have been found to generate hydrogen halides, the stabilizing material alleviates the problem, apparently by interacting with any hydrogen halides to produce a stable material (though the present invention is not limited to any particular mode of action).

DETAILED DESCRIPTION OF THE INVENTION

While the invention will be described in connection with one or more embodiments, it will be understood that the invention is not limited to those embodiments. On the contrary, the invention includes all alternatives, modifications, and equivalents as may be included within the spirit and scope of the appended claims. The mention of or statement of a preference for certain embodiments does not indicate an intent to exclude other embodiments that are not mentioned or stated to be preferred.

The reaction contemplated here broadly relates to the oligomerization of ethylene and other lower olefins to produce higher olefins. In this context, "lower" and "higher" are relative; a lower olefin, as used in this disclosure is any 1-

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olefin that can be converted to a higher 1-olefin, wherein the higher 1-olefin has a greater number of carbon atoms than the lower olefin. The reaction is carried out in the presence of one or more catalysts under conditions encouraging the reaction to proceed.

5 The present invention will be exemplified in the context of a trimerization reaction, although it is contemplated that the invention will find use in other oligomerization reactions. "Trimerization", as used in this disclosure, is defined as any combination of any two, three, or more olefins reducing the number of olefin, i.e., carbon-carbon, double bonds by two. For example, the three olefin
10 bonds in the combination of three ethylene units can be reduced by two, to one olefin bond, in 1-hexene. In another example, the four olefin bonds in the combination of two 1,3-butadiene units can be reduced by two, to two olefin bonds, in 1,5-cyclooctadiene.

 As used here, the term "trimerization" is intended to include
15 dimerization of diolefins, as well as "co-trimerization", each as further discussed below. The reactants, catalysts, equipment, and reaction conditions useful in the present process and the reaction products and by-products formed as a result of the trimerization reaction are further described below.

Reactants

20 The reactants applicable for use in the trimerization process of this invention include olefinic compounds which can self-react, i.e., trimerize, to give useful products. For example, the self-reaction of ethylene can give 1-hexene, and the self-reaction of 1,3-butadiene can give 1,5-cyclooctadiene. The reactants applicable for use in the trimerization process of this invention also include olefinic
25 compounds which can react with other olefinic compounds, i.e., co-trimerize, to give useful products. For example, co-trimerization of ethylene plus hexene can give 1-decene or 1-tetradecene. Co-trimerization of ethylene and 1-butene can give 1-octene. Co-trimerization of 1-decene and ethylene can give 1-tetradecene or 1-docosene.

30 Suitable trimerizable olefin compounds are those compounds having from about 2 to about 30 carbon atoms per molecule and having at least one olefinic double bond. Exemplary olefins include, but are not limited to the

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following.

Acyclic olefins are contemplated such as, for example, ethylene, propylene, 1-butene, 2-butene, isobutylene, 1-pentene, 2-pentene, 1-hexene, 2-hexene, 3-hexene, 1-heptene, 2-heptene, 3-heptene, the four normal octenes, the
5 four normal nonenes, and mixtures of any two or more of those.

Exemplary diolefin compounds contemplated here include, but are not limited to, 1,3-butadiene, 1,4-pentadiene, and 1,5-hexadiene.

If branched or cyclic olefins are used as reactants, while not wishing to be bound by theory, it is believed that steric hindrance could hinder the
10 trimerization process. Therefore, the branched or cyclic portion of the olefin generally will be distant from the carbon-carbon double bond. The present invention is not limited to use with the olefins suggested by this theory to be useful. Any olefin that will participate in the reaction is contemplated for use according to the present invention.

Catalyst Systems

One trimerization catalyst system contemplated in accordance with this invention is a three-part system comprising the combination of a chromium source, a pyrrole-containing compound and a metal alkyl. Optionally, the catalyst system can be supported on an inorganic oxide support. These catalyst systems are
20 especially useful for the dimerization and trimerization of olefins, such as, for example, ethylene to 1-hexene. For present purposes, any catalyst or catalyst system comprising a metal alkyl is more broadly contemplated. The catalyst system commonly includes a halide source, for example, a chloride, bromide, iodide, or fluoride compound.

25 The chromium source can be one or more organic or inorganic compounds, in which the chromium oxidation state is from 0 to 6. Generally, the chromium source will have a formula of CrX_n , in which each X can be the same or different, and can be any organic or inorganic radical, and n is an integer from 1 to 6. Exemplary organic radicals can have from about 1 to about 20 carbon atoms per
30 radical, and can be alkyl, alkoxy, ester, ketone, carboxylate or amido radicals, for example. The organic radicals can be straight-chained or branched, cyclic or acyclic, aromatic or aliphatic, can be made of mixed aliphatic, aromatic, or cycloaliphatic

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groups. Exemplary inorganic radicals include, but are not limited to, any anion or oxidizing radical, for example, halides, sulfates, or oxides.

Preferably, the chromium source is a chromium (II)- or chromium (III)-containing compound that can yield a catalyst system with improved oligomerization or trimerization activity.

Most preferably, the chromium source is a chromium (III) compound because of its ease of use, availability, and enhanced catalyst system activity.

Exemplary chromium (III) compounds include, but are not limited to, chromium carboxylates, chromium naphthenates, chromium halides, chromium pyrrolides, and chromium dionates. Specific exemplary chromium (III) compounds (followed in some instances below by their respective abbreviations) include, but are not limited to chromium (III) 2,2,6,6,-tetramethylheptanedionate – Cr(TMHD)₃; chromium (III) 2-ethylhexanoate – Cr(EH)₃; chromium (III) tris-(2-ethylhexanoate); chromium (III) naphthenate – Cr(Np)₃; chromium (III) chloride; chromic bromide; chromic fluoride; chromium (III) acetylacetonate; chromium (III) acetate; chromium (III) butyrate; chromium (III) neopentanoate; chromium (III) laurate; chromium (III) stearate; chromium (III) pyrrolide; chromium (III) oxalate; or combinations of two or more.

Specific exemplary chromium (II) compounds include, but are not limited to chromous bromide; chromous fluoride; chromous chloride; chromium (II) bis-(2-ethylhexanoate); chromium (II) acetate; chromium (II) butyrate; chromium (II) neopentanoate; chromium (II) laurate; chromium (II) stearate; chromium (II) oxalate; chromium (II) pyrrolides; or combinations of two or more. Chromium (II) and chromium (III) compounds can also be combined.

The pyrrole-containing compound of the catalyst system can be any one, two or more of those that will react with a chromium source to form a chromium pyrrolide complex. As used in this disclosure, the term "pyrrole-containing compound" refers to hydrogen pyrrolide (i.e. pyrrole -- C₄H₅N), derivatives of hydrogen pyrrolide, and substituted pyrrolides, as well as metal pyrrolide complexes and mixtures thereof. A "pyrrolide" is defined as a compound comprising a 5-membered, nitrogen-containing heterocycle.

Broadly, the pyrrole-containing compound can be pyrrole or any heteroleptic or homoleptic metal complex or salt containing a pyrrolide radical or

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ligand. The pyrrole-containing compound can be either affirmatively added to the reaction or generated in-situ.

Generally, the pyrrole-containing compound will have from about 4 to about 20 carbon atoms per molecule. Exemplary pyrrolides, mentioned because of their high reactivity and activity with the other reactants, include pyrrole; lithium pyrrolide; sodium pyrrolide; potassium pyrrolide; cesium pyrrolide; the salts of substituted pyrrolides; or combinations thereof. The useful substituted pyrrolides include, but are not limited to pyrrole-2-carboxylic acid; 2-acetylpyrrole; pyrrole-2-carboxaldehyde; tetrahydroindole; 2,5-dimethylpyrrole; 2,4-dimethyl-3-ethylpyrrole; 3-acetyl-2,4-dimethylpyrrole; ethyl-2,4-dimethyl-5-(ethoxycarbonyl)-3-pyrrole-propionate; ethyl-3,5-dimethyl-2-pyrrolecarboxylate; or combinations thereof. When the pyrrole-containing compound contains chromium, the resultant chromium compound can be called a chromium pyrrolide.

The most preferred pyrrole-containing compounds useful in a trimerization catalyst system can be selected from the group consisting of hydrogen pyrrolide, 2,5-dimethylpyrrole or chromium pyrrolides because of enhanced trimerization activity. Optionally, for ease of use, a chromium pyrrolide can provide both the chromium source and the pyrrole-containing compound. As used in this disclosure, when a chromium pyrrolide is used to form a catalyst system, a chromium pyrrolide is considered to provide both the chromium source and the pyrrole-containing compound. While all pyrrole-containing compounds can produce catalyst systems with high activity and productivity, use of pyrrole or 2,5-dimethylpyrrole can produce a catalyst system with enhanced activity and selectivity to a desired product.

The metal alkyl of the catalyst system can be any heteroleptic or homoleptic metal alkyl compound. One or more metal alkyls can be used. The alkyl ligands on the metal can be aliphatic, aromatic, or both (if more than one ligand is present). Preferably, the alkyl ligands are any saturated or unsaturated aliphatic radical.

The metal alkyl can have any number of carbon atoms. However, due to commercial availability and ease of use, the metal alkyl will usually comprise less than about 70 carbon atoms per metal alkyl molecule and preferably less than

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about 20 carbon atoms per molecule.

Exemplary metal alkyls include, but are not limited to, alkylaluminum compounds, alkylboron compounds, alkylmagnesium compounds, alkylzinc compounds or alkyl lithium compounds. Exemplary metal alkyls include, but are not limited to n-butyl lithium; s-butyllithium; t-butyllithium; diethylmagnesium; diethylzinc; triethylaluminum; trimethylaluminum; triisobutylaluminum; or combinations thereof.

Preferably, the metal alkyl is selected from the group consisting of non-hydrolyzed, i.e., not pre-contacted with water, alkylaluminum compounds, derivatives of alkylaluminum compounds, halogenated alkylaluminum compounds, and mixtures thereof. Mixed metal alkyls can provide improved product selectivity, as well as improved catalyst system reactivity, activity, or productivity. The use of hydrolyzed metal alkyls can result in decreased olefin (i.e. liquid) production and increased polymer (i.e. solid) production.

Most preferably, the metal alkyl is a non-hydrolyzed alkylaluminum compound expressed by the general formulas AlR_3 , AlR_2X , $AlRX_2$, AlR_2OR , $AlRXOR$, or $Al_2R_3X_3$, in which Al is an aluminum atom, each R is an alkyl group, O is an oxygen atom, and X is a halogen atom. Exemplary compounds include, but are not limited to triethylaluminum; tripropylaluminum; tributylaluminum; diethylaluminum chloride; diethylaluminum bromide; diethylaluminum ethoxide; diethylaluminum phenoxide; ethylaluminum dichloride; ethylaluminum sesquichloride; and mixtures thereof for best catalyst system activity and product selectivity. The most preferred single alkylaluminum compound is triethylaluminum, for the best catalyst system activity and product selectivity. Catalyst systems most pertinent to the present invention comprise aluminum alkyls containing a halide, such as a chloride or a bromide.

While not wishing to be bound by theory, it is believed that a chloride containing-compound can improve product purity and selectivity. Any chloride-containing compound can be used, such as, for example, DEAC and organochlorides. Exemplary organochlorides include, but are not limited to, carbon tetrachloride, methylene chloride, chloroform, benzylchloride, 1-hexachloroethane and mixtures thereof.

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One particular composite catalyst contemplated here is the combination of chromium (III) ethylhexanoate, 2,5-dimethylpyrrole, triethylaluminum, and diethylaluminum chloride. This composite catalyst system can be used to trimerize ethylene, forming 1-hexene. U.S. Patent No. 5,198,563 teaches the use of a suitable trimerization catalyst for the present invention. The entire patent is incorporated by reference for its disclosure of trimerization catalysts.

Media

Usually, the chromium source, the pyrrole-containing compound, and the metal alkyl are combined in an olefinically or aromatically unsaturated hydrocarbon reaction medium. The hydrocarbon can be any aromatic or aliphatic hydrocarbon, in a gaseous, liquid or solid state. Preferably, to thoroughly contact the chromium source, pyrrole-containing compound, and metal alkyl, the hydrocarbon is in a liquid state.

The hydrocarbon can have any number of carbon atoms per molecule. Usually, the hydrocarbon will comprise less than about 70 carbon atoms per molecule, and preferably, less than about 20 carbon atoms per molecule, due to the commercial availability and ease of use of low-molecular-weight compounds. The most preferred hydrocarbon compound is a reaction product formed by use of the catalyst system. For example, if 1-hexene is a reaction product, some of the 1-hexene product can be recycled for use as a reaction medium.

Exemplary unsaturated aliphatic hydrocarbon compounds contemplated for use as catalyst reaction media include, but are not limited to, ethylene, 1-hexene, 1,3-butadiene, and mixtures thereof. Exemplary unsaturated aromatic hydrocarbons useful as reaction media include, but are not limited to, benzene, toluene, ethylbenzene, xylene, mesitylene, hexamethylbenzene, and mixtures thereof. Unsaturated aromatic hydrocarbons are preferred to improve the stability of the catalyst system and to produce a highly active and selective catalyst system. The most preferred unsaturated aromatic hydrocarbon is ethylbenzene for best catalyst system activity and product selectivity.

The trimerization process generally is carried out in a slurry of the catalyst components in an inert medium or diluent. Broadly, the common trimerization reaction diluents can be liquid paraffins, cycloparaffins, olefins or

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aromatic hydrocarbons. Exemplary reactor diluents include, but are not limited to, isobutane, cyclohexane, and methylcyclohexane. Isobutane can be used for enhanced compatibility with known olefin polymerization processes. However, a homogenous trimerization catalyst system is more easily dispersed in cyclohexane.

5 Therefore, a preferred diluent for a homogeneous catalyzed trimerization process is cyclohexane.

In accordance with another embodiment of this invention, a slurry process can be carried out in a diluent (medium), which is a product of the olefin oligomerization process. Therefor, the choice of reactor diluent, or medium, is based on the selection of the initial olefin reactant. For example, if the
10 oligomerization catalyst is used to trimerize ethylene to 1-hexene, the solvent for the oligomerization reaction would be 1-hexene. If ethylene and hexene were trimerized to produce 1-decene, the oligomerization reaction solvent would be 1-decene. If 1,3-butadiene was trimerized to 1,5-cyclooctadiene, the trimerization
15 reactor solvent would be 1,5-cyclooctadiene.

The catalyst system comprising a chromium source, pyrrole-containing compound, metal alkyl, and reaction media can contain additional components that do not adversely affect and can enhance the resultant catalyst system, such as, for example, halides.

20 Equipment

The trimerization reaction can be conveniently carried out in a suitable reactor, preferably a continuous-feed autoclave reactor with a fluid jacket or internal heat transfer coil and any suitable stirring mechanism, such as, for example, mechanical stirring or an inert gas, typically nitrogen, purge, piping and valves. Any
25 other suitable reaction equipment may also be used. For example, a loop reactor with mechanical stirring, such as, for example, a stirring pump, can be used

Reaction Conditions

Trimerization reaction products, as defined in this specification, can be prepared from catalyst systems of this invention by dispersion reaction, slurry
30 reaction, or gas phase reaction techniques using conventional equipment and contacting processes. Contacting of the monomer or monomers with a catalyst system can be effected by any manner known in the art. One convenient process is

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to suspend the catalyst system in the reaction medium and to agitate the mixture to maintain the catalyst system in dispersion throughout the trimerization process.

Other known contacting processes also can be employed.

Commonly, the catalyst system and reaction media are introduced to the reactor either continuously or in one or more charges, and the olefin reactant is continuously or intermittently introduced throughout the reaction as a gas under pressure. The pressure in the reactor usually is maintained by adding a gaseous olefin reactant at a suitable rate to replace the olefin consumed by the reaction.

Hydrogen gas can be charged to the reactor during the reaction to improve the rate of reaction and enhance the catalyst system activity and trimer product selectivity. The presence of hydrogen can be advantageous for reducing the by-product polymers into a powdery, non-tacky form that is easily removed from the reactor and easily separated from the effluent, as by filtering and/or evaporation. The partial pressure of hydrogen present is usually from about 0.1 to about 100 kg/cm² (about 1 to 1000 N/cm²), preferably from about 0.1 to about 80 kg/cm² (about 1 to 800 N/cm²).

The reaction temperature employed can be any temperature that can trimerize the olefin reactants. Generally, reaction temperatures are within a range of from about 0°C to about 250°C. Preferably, reaction temperatures within a range of from about 60°C to about 200°C, and most preferably within a range of from about 80°C to about 150°C are employed. When the reactant is predominately ethylene, a temperature in the range of from about 0°C to about 300°C generally can be used. Preferably, when the reactant is predominately ethylene, a temperature in the range of from about 60°C to about 110°C is employed. If the reaction temperature is too low, the polymer tends to stick to the reactor surfaces. If the reaction temperature is too high, the catalyst system and reaction products may decompose.

The overall reaction pressure employed can be any pressure that can trimerize the olefin reactants. Generally, reaction pressures are within a range of from about atmospheric pressure (0 psig or 0 N/cm² gauge pressure) to about 2500 psig (about 1700 N/cm² gauge pressure). Preferably, reaction pressures within a range of from about atmospheric pressure to about 1000 psig (690 N/cm² gauge pressure), and most preferably within a range of 300 to 900 psig (about 200 to

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about 620 N/cm² gauge pressure), are employed. If the reaction pressure is too low, the catalyst system activity can be too low. The maximum pressure generally is dictated by safety concerns and the desire for vessels having walls no thicker than necessary.

5 The contents of the reactor can be agitated or stirred by an inert gas (e.g. nitrogen) purge, by introducing the reactant, hydrogen, fluid medium, or catalyst or exhausting the effluent in a manner causing agitation, by mechanical or magnetic stirring, or in any other suitable manner.

10 The reaction usually is run continuously by steadily charging lower 1-olefin reactant(s), catalyst system, and process medium and removing the liquid contents of the reactor. For example, a continuous stirred tank reactor system can be employed that includes feed systems for catalyst system, reactant and medium and a discharge system for the effluent. A batch process can also be employed, however.

15 The reactor effluent is treated to kill the remainder of the catalyst system, separate products, recycle the residual reactants, medium, and other components suitable for recycling, and dispose of any components that are not recycled.

20 The trimerization reaction is exothermic, so the reaction temperature usually can be regulated by circulating cooling water through a jacket or heat transfer coil, thus transferring heat out of the reactor. It is important to be able to transfer heat efficiently out of the reactor, so the reactor can be effectively maintained at the desired reaction temperature and the heat can be removed using a minimum quantity of the cooling medium. Another advantage of more effective
25 heat transfer is that the trimerization reaction can be run at a higher throughput for a given temperature, which can improve production efficiency.

30 After the catalyst system has been used to prepare one or more olefin products, the reactor effluent stream comprising olefin trimer product(s), catalyst system, and some polymer or higher oligomer by-products, is contacted with a catalyst kill agent to "kill", deactivate or quench the catalyst. Exemplary catalyst kill agents contemplated here are alcohols, primary or secondary amines, or alkanolamines.

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Any alcohol that can be easily dispersed in the reactor effluent stream can be used as a catalyst kill agent. For example, lower alcohols such as methanol, ethanol, propanol, isopropanol, etc. can kill the catalyst system. Preferably, however, an alcohol is selected that has a boiling point, or molecular weight, such that the alcohol will not form an azeotrope with the olefin monomer product. Generally, materials with similar boiling points and similar molecular weights are more likely to form azeotropes.

In an exemplary process, in which the catalyst system is used to trimerize ethylene to 1-hexene, a monofunctional alcohol with six or more carbon atoms per molecule is preferred as the catalyst kill agent. Most preferably, a monofunctional alcohol having six to twelve carbon atoms per molecule is used for best catalyst system quenching. Such alcohols are easily removable from the 1-hexene olefin product. Exemplary monofunctional alcohols include, but, are not limited to 1-hexanol; 2-hexanol; 3-hexanol; 2-ethyl-1-hexanol; 3-octanol; 1-heptanol; 2-heptanol; 3-heptanol; 4-heptanol; 2-methyl-3-heptanol; 1-octanol; 2-octanol; 3-octanol; 4-octanol; 7-methyl-2-decanol; 1-decanol; 2-decanol; 3-decanol; 4-decanol; 5-decanol; 2-ethyl-1-decanol; and mixtures thereof.

Alternatively, a low-molecular-weight diol or polyol, for example ethylene glycol, can be used as a catalyst kill agent. Diols and polyols commonly have much higher boiling points than monoalcohols of comparable molecular weight, and thus can be separated more easily from 1-hexene.

The alcohol is used in an amount at least partially effective to quench the catalyst. For example, alcohol may be added in a molar ratio of from about 0.01 to about 100, preferably from about 0.01 to about 10, most preferably from about 0.05 to about 2, in relation to the metal content of the catalyst to be deactivated.

If an alcohol is used as the catalyst kill agent for a halogenated catalyst system, hydrogen halides can be generated, as described previously. Practitioners that manufacture higher olefins commonly will elect to avoid or reduce the production of hydrogen halides. The hydrogen halide problem can be addressed by treating the product stream with a stabilizing material that forms a stable halide or hydrogen halide salt.

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The stabilizing material contemplated here can be an aliphatic amine, an aromatic amine, a metal salt of an amide, a metal salt of a butoxide, a metal salt of a carboxylic acid, or a combination of these materials. More specifically, the stabilizing material in the present invention can be selected from cyclic and acyclic, aromatic and aliphatic amines, nitriles, amides, etc.

The primary amines contemplated as stabilizing materials include ethylamine; isopropylamine; cyclohexylamine; benzylamine; naphthylamine; and others. The secondary amines include diethylamine; diisopropylamine; dibutylamine; dicyclohexylamine; dibenzylamine, and bis(trimethylsilyl)amine. The stabilizing material can be a tertiary amine such as tributylamine.

The cyclic and aromatic amines and related compounds contemplated here as stabilizing materials include aniline; pyridine; dimethylpyridine; morpholine; imidazole; indoline; indole; pyrrole; 2,5-dimethylpyrrole; 3,4-dimethylpyrrole; 3,4-dichloropyrrole; 2,3,4,5-tetrachloropyrrole; 2-acetylpyrrole; pyrazole; pyrrolidine; pyrrolidone, and dipyrrolylmethane.

The stabilizing materials contemplated here can be alkanolamines. One particular advantage of alkanolamines is that the same molecule possesses both alcohol functionality and amine functionality, which may contribute both to deactivating, or killing, the catalyst system and to stabilize against the generation of corrosive hydrogen halides. Exemplary alkanolamines include isopropanolamine, monoethanolamine, diethanolamine, and triethanolamine.

The stabilizing materials contemplated here also include polyamines. Exemplary polyamines are ethylenediamine, diethylenetriamine, and tetramethylethylenediamine.

The metal salts of amides usable in the present invention as stabilizers include salts of, for example, dimethylformamide; N-methylformamide; acetamide; N-methylhexaneamide; succinamide; maleamide; N-methylbenzamide; imidazole-2-carboxamide; di-2-thenolamine; beta-lactam; delta-lactam, or epsilon-lactam with metals of IA, IIA or IIIB Group of the periodic table. Examples of such metal amides are lithium amide; sodium ethylamide; calcium diethylamide; lithium diisopropylamide; potassium benzylamide; sodium bis (trimethylsilyl)amide; lithium indolide; sodium pyrrolide; lithium pyrrolide; potassium pyrrolide;

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potassium pyrrolidide; diethylaluminum pyrrolide; ethylaluminum dipyrrolide; aluminum tripyrrolide; sodium 2,5-dimethylpyrrolide; lithium 2,5-dimethylpyrrolide; potassium 2,5-dimethylpyrrolide; potassium 2,5-dimethylpyrrolidide; diethylaluminum; 2,5-dimethylpyrrolide; ethylaluminum; di(2,5-dimethylpyrrolide);
5 aluminum tri(2,5-dimethylpyrrolide), and combinations of those.

The imides usable in the present invention as stabilizers include 1,2-cyclohexanedicarboxyimide, succinimide, phthalimide, maleimide, 2,4,6-piperidinetriene, and perhydroazines-2,10-dione.

The metal salts of butoxides usable herein are the butoxide salts of
10 alkali metals (describe further). An exemplary butoxide salt is potassium tert-butoxide.

The metal salts of carboxylic acids useful herein as stabilizers include the metal salts, more particularly the lithium, sodium, potassium and/or rubidium salts of, carboxylic acids. Examples of the carboxylic acids include acetic acid,
15 propionic acid, butyric acid, valeric acid, hexanoic acid, heptanoic acid, octanoic acid, nonanoic acid, decanoic acid, benzoic acid, phenylacetic acid, phthalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, acrylic acid, maleic acid, fumaric acid, and salicylic acid. An exemplary carboxylic acid salt contemplated here is silver acetate, lithium acetate, sodium acetate, potassium acetate, and
20 mixtures thereof.

Exemplary phosphines useful herein as stabilizers include tributylphosphine oxide and triethylphosphine.

The stabilizing material should be provided in an amount effective to at least reduce the generation of hydrogen halide gas. For example, from about
25 0.01 to about 100 moles, preferably from about 0.01 to about 10 moles, more preferably from 0.05 to 2 moles of the stabilizing material can be added per mole of halogen in the catalysts.

The use of an alcohol is not essential to quench or kill the catalyst. Other materials, for example primary or secondary amines, can be used to kill a
30 catalyst, either alone or in combination with one or more alcohols. Generally, an aliphatic primary amine, an aliphatic secondary amine, or a combination of those materials is contemplated for use as a catalyst kill agent. More specifically, the

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amines may be acyclic aliphatic amines or cyclic aliphatic amines, within the scope of the invention.

As with the alcohol, the amine quenching material can be provided in an amount effective to at least substantially quench the catalyst, either alone or
5 when combined with an alcohol or other quenching agent.

Enough of the catalyst kill agent is added to the reactor effluent stream to at least substantially quench, deactivate, or "kill", the olefin production catalyst system and to reduce or eliminate the production of undesirable solids, particularly polymer or catalyst solids. If an insufficient amount of catalyst kill
10 agent is used, any metals in the catalyst system, such as chromium or aluminum, can precipitate and interfere with future effluent processing. Generally, up to about five molar equivalents of catalyst kill agent can be added, per mole of metals in the effluent stream. Preferably, the amount of catalyst kill agent added is from about one to about four molar equivalents, and most preferably the amount of catalyst kill
15 agent added is from about two to about three molar equivalents of catalyst kill agent per mole of metals in the reactor effluent stream. Too much catalyst kill agent can cause corrosion of the reactor.

After the catalyst system has been quenched and treated to stabilize any halides, the olefin products, such as, for example, 1-hexene, can be removed.
20 Any removal process can be used, although distillation is preferred for ease of use. In a simple distillation, ethylene is removed from the reaction product, then 1-hexene and the medium are distilled away from the reaction dispersion while the catalyst components are concentrated and recovered together with the by-product polyethylene. Typical distillation temperatures in the distillation kettles are about
25 190°C to about 210°C. These distillation temperatures are believed to be sufficient to promote the decomposition of aluminum halides present in the spent catalyst to produce hydrogen halides, unless steps are taken as described in this disclosure to prevent hydrogen halide generation.

The concentrated dispersion containing by-product polymer and
30 catalyst components may be discarded, or can be further treated as described below.

The product stream produced by the ethylene trimerization process commonly contains one of more of the following compounds butene; 1-hexene;

internal hexenes (i.e. 2-hexene or 3-hexene); octenes; decenes; reaction medium; and "heavies".

The waste product steam formed by removing the desired olefin monomer products can be further processed by contacting it with an aqueous base to
5 remove metals. Organic bases are not preferred at this point because organic bases can be too weak to precipitate heavy metals, such as chromium. The preferred aqueous inorganic bases are sodium hydroxide and potassium hydroxide, due to their ease of use, availability, low cost, and beneficial effects on future processing.

The amount of aqueous inorganic base added can be any amount
10 sufficient to precipitate most or substantially all of the chromium. The most important goal of this step is to remove chromium or other heavy metals, as any remaining dispersed aluminum does not raise the same environmental issues.

Addition of too much or too little of the aqueous inorganic base can prevent precipitation of the chromium. Generally, about up to about 4 molar
15 equivalents of aqueous inorganic base should be used per mole of chromium and aluminum. Preferably, from about 0.2 to about 3 molar equivalents, and most preferably from about 1 to 2 molar equivalents of the aqueous inorganic base should be used per mole of chromium and aluminum. The chromium-containing solid precipitate then can be removed and disposed of properly.

20 Following removal of the chromium containing solid precipitate, the aqueous and organic layers, or portions, are separated. The organic layer can be disposed of.

Removing Residues

The trimerization process commonly produces two residues that can
25 build up on the internal surfaces of the reactor.

One residue, long recognized to build up on the walls of the reactor, is an oligomer or a polymer having a chain length higher than the intended product, formed as a by-product. This higher oligomer or polymer residue is referred to here, for the sake of simplicity, as just "polymer residue". For example, in the case
30 of an ethylene reaction, polyethylene or paraffin wax residue can be formed and build up on the internal surfaces of the reactor. This polymer residue detracts from the heat transfer efficiency of the internal surfaces of the reactor.

Polymer residue may be removed from the reactor by washing the reactor with a solvent for the residue. The trimerization reactor commonly is supplied with a solvent for by-product polymers – such as cyclohexane or methylcyclohexane – as the process medium. When a polymer solvent is used as the process medium, the same process medium can be used to periodically flush out the reactor. The washing conditions can be more stringent than the usual process conditions, to remove the polymer residue that is not removed under the usual process conditions. For example, the washing step can be a "hot wash", carried out by circulating the usual process medium at a higher temperature than the process temperature to melt, more quickly dissolve, or otherwise dislodge the polymer residue.

In a continuous ethylene trimerization process, the hot wash can be carried out as follows. The reaction can be halted by stopping the feed of catalyst and reactants while continuing to inject and drain the reactor medium, which can be, but is not limited to, cyclohexane and/or methylcyclohexane and increasing the medium temperature by about 60°C to 70°C. The hot wash is continued for several hours, or as long as necessary to remove all or substantially all of the polymer residue. This hot wash has been found to remove the buildup of the polymer residue.

A second residue, which also detracts substantially from the heat transfer efficiency of the reactor, is referred to here as catalyst residue. The exact chemical constitution of this catalyst residue is not known. It may be a precipitate or deposit of the entire catalyst or one or more of the catalyst ingredients, the product of a reaction between the catalyst ingredients, the catalyst and the reactor wall, spent catalyst constituents, a combination of these residues, or something else. The residue is believed to be associated with the catalyst, though the present invention is not limited by the accuracy of that theory.

A further understanding of how to make and use the present invention and its advantages will be provided by reference to the following examples.

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EXAMPLES

Example 1

To an inert gas purged one liter, three-necked flask equipped with nitrogen purge, magnetic stirrer, glass column, Dean-Stark tube and condenser was added 250 mL dry dodecane and 260 mL of 2-ethyl-1-hexanol. The system was purged again for 20 minutes and 50 mL of selective 1-hexene catalyst (5 mg Cr/mL) was added. Water (2 mL) was added and the system was heated to reflux. Nine samples were taken over 5 hours. Acidity was assessed by water extraction of the samples taken from the Dean Stark tube and testing the water with pH paper. The first sample was mildly acidic and all of the other samples were very acidic. Water was observed to be present in the last sample.

Example 2

Example 1 was repeated but in addition to the 2 mL of water, 4 mL of tri-n-butylamine also was added. None of the subsequent nine samples from the Dean-Stark tube were acidic demonstrating the effectiveness of adding an amine to the process. Water was observed in the ninth sample, as was observed in Example 1. The presence of the amine removed all indications of acidity.

Experimental Apparatus for Examples 3 and 4

The apparatus used for Examples 3 and 4 was a one liter, three-necked round bottom flask equipped with a glass well for a thermocouple to monitor the kettle temperature, an addition funnel and a Dean-Stark tube. A condenser was placed at the top of the Dean-Stark tube as was a thermocouple to measure overhead temperature and a wire that held a piece of pH paper at the top of the Dean-Stark tube. The flask also was equipped with a magnetic stirring bar and a stirrer and a heating mantle. A nitrogen stream constantly swept material through the apparatus and a bubbler containing water.

General Procedure for Examples 3 and 4

In a typical experiment, 200 g dodecane was added to the flask and the system purged with nitrogen. Diethylaluminum chloride (DEAC) (1.9M) in dodecane then was charged to the flask from a metal cylinder. The desired amount of 2-ethyl-1-hexanol was then added slowly and allowed to react. The temperature would rise to approximately 50-70°C and gas evolution was observed. The contents

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were stirred for 30 minutes to allow complete reaction and the kettle sampled. The contents then were heated to reflux. Overhead was removed as necessary to obtain the desired kettle temperature. The overhead was sampled (about 2 mL) periodically from the Dean-Stark tube.

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Example 3

The following materials were added to the apparatus described above: 200 g of dry dodecane, 80.8 mL of a 1.9M solution of DEAC in dodecane and 96 mL of 2-ethyl-1-hexanol was slowly added. This mixture was heated to a kettle temperature of 170°C to 209°C over 2.75 hours. The following observations were made. Immediately after the addition of the alcohol, there was no change in color of the pH paper in the top of the Dean-Stark tube and the pH of the water bubbler was neutral. Upon heating, the pH paper in the Dean-Stark tube turned reddish-purple (strongly acidic). Samples from the bottom of the Dean-Stark tube turned moist pH paper to indicate acidity and the test for chloride with silver acetate was positive. It was clear that the acidic hydrochloric acid was present.

15

Example 4

The following materials were added to the apparatus described above: 200 g of dry dodecane, 81 mL of a 1.9M solution of DEAC in dodecane and 96 mL of 2-ethyl-1-hexanol was slowly added. Tri-n-butylamine (40.25 g) was added. This mixture was heated to a kettle temperature of 208°C over 4 hours. The following observations were made. There was no change in color of the pH paper in the top of the Dean Stark tube throughout the experiment. The pH of the water bubbler was neutral at the end of the experiment. Samples from the bottom of the Dean Stark tube were neutral or slightly basic as indicated by moist pH paper. It was clear that any acid formed was removed from the system by the addition of the amine.

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While this invention has been described in detail for the purpose of illustration, it is not to be construed as limited thereby but is intended to cover all changes and modifications within the spirit and scope thereof.

CLAIMS

1. An oligomerization process comprising:
 - a) providing at least one catalyst system, at least one lower olefin, and at least one process medium;
 - 5 b) reacting said lower olefin in the presence of said catalyst system to produce a product stream comprising a higher olefin product and a catalyst system residue dispersed in said process medium;
 - c) treating said product stream with a quenching material comprising an aliphatic primary amine, an aliphatic secondary amine, an aliphatic tertiary
10 amine, or a combination of those materials, said quenching material being provided in an amount effective to at least substantially quench said catalyst system.
2. A process according to claim 1, wherein said quenching material comprises an acyclic aliphatic amine.
3. A process according to claim 1, wherein said quenching material
15 comprises a cyclic aliphatic amine.
4. A process according to claim 1, wherein said quenching material comprises a primary amine.
5. A process according to claim 1, wherein said quenching material comprises a secondary amine.
- 20 6. A process according to claim 1, wherein said quenching material comprises cyclohexylamine.
7. A process according to claim 1, wherein said quenching material comprises dibutylamine.
8. A process according to claim 1, wherein said quenching material
25 comprises an alkanolamine.
9. A process according to claim 1, wherein said quenching material comprises isopropylamine.
10. A process according to claim 1, wherein said quenching material comprises monoethanolamine.
- 30 11. A process according to claim 1, wherein said quenching material comprises diethanolamine.
12. A process according to claim 1, wherein said quenching material is

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separable from said higher olefin by distillation.

13. A process according to claim 1, wherein said quenching material further comprises an alcohol.

14. A process according to claim 1, wherein said quenching material is added in a molar ratio of from about 1 to about 5, in relation to the metal content of said catalyst.

15. An oligomerization process comprising:

a) providing a halogenated catalyst system, a lower olefin, and a process medium;

b) reacting said lower olefin in the presence of said catalyst system to produce a product stream comprising a higher olefin product and a catalyst system residue dispersed in said process medium;

c) treating said product stream with an alcohol in an amount effective to at least partially quench said catalyst system; and

d) treating said product stream with a stabilizing material that forms a stable hydrogen halide salt, said stabilizing material being provided in an amount effective to reduce the generation of hydrogen halide gas.

16. A process according to claim 15, wherein said stabilizing material is selected from an aliphatic amine, an aromatic amine, a metal salt of an amide, a metal salt of a butoxide, a metal salt of a carboxylic acid, or a combination of those materials.

17. A process according to claim 15, wherein said stabilizing material comprises an acyclic aliphatic amine.

18. A process according to claim 15, wherein said stabilizing material comprises a cyclic aliphatic amine.

19. A process according to claim 15, wherein said stabilizing material comprises an aromatic amine.

20. A process according to claim 15, wherein said stabilizing material comprises a primary amine.

21. A process according to claim 15, wherein said stabilizing material comprises a secondary amine.

22. A process according to claim 15, wherein said stabilizing material

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comprises a tertiary amine.

23. A process according to claim 15, wherein said stabilizing material comprises an alkanolamine.

24. A process according to claim 15, wherein said stabilizing material
5 comprises isopropylamine.

25. A process according to claim 15, wherein said stabilizing material comprises monoethanolamine.

26. A process according to claim 15, wherein said stabilizing material comprises diethanolamine.

10 27. A process according to claim 15, wherein said stabilizing material comprises cyclohexylamine.

28. A process according to claim 15, wherein said stabilizing material comprises dibutylamine.

15 29. A process according to claim 15, wherein said stabilizing material comprises tributylamine.

30. A process according to claim 15, wherein said stabilizing material comprises ethylenediamine.

31. A process according to claim 15, wherein said alcohol has at least six carbon atoms per molecule.

20 32. A process according to claim 15, wherein said alcohol and said stabilizing material are separable from said higher olefin by distillation.

33. A process according to claim 15, wherein said alcohol is 2-ethylhexanol.

25 34. A process according to claim 15, wherein said alcohol is added in a molar ratio of from about 0.01 to about 100, in relation to the metal content of said catalyst.

35. A process according to claim 15, wherein said stabilizing material is added in a molar ratio of from about 0.01 to about 100, in relation to the metal content of said catalyst.

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/US00/35366

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : C07C 2/06, 2/08, 2/24, 2/26
US CL : 585/511, 512, 513, 527, 952

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
U.S. : 585/511, 512, 513, 527, 952

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EAST search terms: oligomerization, quench, amine, chromium, pyrrole, polymerization, catalyst, inhibit, deactivate

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 200 654 A1 (CHAUVIN et al) 10 December 1986 (10.12.1986), see column 1, line 44 through column 2, line 50	1-12, 14
---		13, 15-35
Y		13
Y	US 5,030,790 A (SERGIENKO et al) 09 July 1991 (09.07.1991), see column 2, line 7-37 and column 3, line 24 through column 4, line 64.	
Y	US 5,689,028 A (LASHIER et al) 18 November 1997 (18.11.1997), see column 1, line 55 through column 6, line 26.	15-35

☐ Further documents are listed in the continuation of Box C.

☐ See patent family annex.

* Special categories of cited documents.

- A- document defining the general state of the art which is not considered to be of particular relevance
- E- earlier application or patent published on or after the international filing date
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- O- document referring to an oral disclosure, use, exhibition or other means
- P- document published prior to the international filing date but later than the priority date claimed

- T- later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- X- document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- Y- document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- &- document member of the same patent family

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